

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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Title : A METHOD FOR ISOMERIZING  
: HALOGENATED AROMATICS



22469

PATENT TRADEMARK OFFICE

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**PRELIMINARY AMENDMENT**

Commissioner for Patents  
Washington, DC 20231

Sir:

Prior to action on the merits of the case, kindly amend the above-identified application as follows:

**In the Specification**

**In the Title:**

~~A CATALYST COMPOSITION AND~~ A METHOD FOR ISOMERIZING  
HALOGENATED AROMATICS

**On Page 5, Third Paragraph:**

Moreover, the inventors investigated ~~on~~ the method for isomerizing halogenated aromatics, and as a result, found that if halogenated aromatics with a dissolved oxygen content of 15 wt ppm or less are used, the deactivation of the zeolite-containing catalyst can be inhibited, to prolong the life of the catalyst, for allowing efficient isomerization of halogenated aromatics.

## On Page 6, First Paragraph:

The present invention is ~~going to achieve~~ achieves the above objects. The catalyst composition for isomerizing halogenated aromatics of the present invention is a catalyst composition for isomerizing halogenated aromatics, characterized in that the maximum diameter of secondary particles of the zeolite in the formed catalyst is 5 microns or less. The isomerizing catalyst composition of the present invention includes the following preferable embodiments.

## On Page 11, First Paragraph

Mordenite is a zeolite which gives an X-ray diffraction pattern shown in Table 1 below.

[Table 1]

X-ray diffraction pattern of mordenite

Lattice spacing	d(Å)	Intensity
13. 6	±0. 2	M
10. 2	±0. 2	W
9. 0	±0. 2	S
6. 56	±0. 1	S
6. 40	±0. 1	M
6. 05	±0. 1	W
5. 80	±0. 1	M
4. 52	±0. 08	M
3. 99	±0. 08	S
3. 83	±0. 08	W
3. 76	±0. 08	W
3. 53	±0. 05	W
3. 46	±0. 05	VS
3. 38	±0. 05	S
3. 28	±0. 05	W
3. 20	±0. 05	S
3. 15	±0. 05	W
2. 89	±0. 05	M
2. 51	±0. 05	W

## **On Page 11, Fifth Paragraph**

As a general trend, the primary particle size of mordenite tends to be smaller if an a nitrogen containing organic base such as tetraethylammonium hydroxide or a surfactant such as polyethylene glycol is present in the reaction mixture, though this cannot be generally said since the primary particle size is affected variously by the reaction mixture composition at the time of synthesis, crystallization temperature, crystallization time, stirring speed, etc. Furthermore, for the composition ratios in the reaction mixture, since the particle size complicatedly changes, depending on the silica and alumina contents and alkali concentration, it is preferable to select the optimum composition ratios. As for crystallization conditions, if the crystallization temperature is lower, or if the crystallization time is shorter, or if the stirring speed is higher, the primary particle size tends to be smaller. Irrespective of the method, in the present invention it is only required that mordenite is 0.2 micron or less in the longest axes of its primary particles.

## **On Page 21, Fifth Paragraph**

The slurry was heated at 160°C for 72 hours with stirring (250 rpm) in a 1-liter autoclave. The reaction product was washed with distilled water and filtered five times and then dried overnight at about 120-C. Thus there was obtained a pentasil-type zeolite which gives an X-ray diffraction pattern shown in Table 2 below and has the silica/alumina molar ratio of 21.9.

[Table 2]

X-ray diffraction pattern of pentasil-type zeolite

Lattice spacing	d(Å)	Intensity
11. 2	±0. 2	VS
10. 1	±0. 2	S
9. 8	±0. 2	M
6. 37	±0. 1	W
6. 00	±0. 1	W
5. 71	±0. 1	W
5. 58	±0. 1	W
4. 37	±0. 08	W
4. 27	±0. 08	W
3. 86	±0. 08	VS
3. 82	±0. 08	VS
3. 75	±0. 08	S
3. 72	±0. 08	S
3. 66	±0. 05	M
3. 00	±0. 05	M
2. 00	±0. 05	W

## Page 22 , Second Paragraph:

The formed pellet (30 g dry base) was treated with 10 wt% aqueous solution of ammonium chloride at 80-85°C for 1 hour. The ion-exchange treatment was repeated 5 times in the same manner as above. The treatment was followed by rinsing with distilled water 5 times. It was dried overnight at 120°C, to obtain an ammonium ion-exchanged formed pellet. Then, it was calcined at 550°C for 2 hours, to convert ammonium ions into hydrogen ions. Thus, there was obtained a catalyst compound A, which contained an acid type zeolite, the aperture of the largest pore of which comprised the 10-membered oxygen ring. SEM observation shows that the maximum diameter of secondary particles of the zeolite in the catalyst was 3 microns. An observed SEM image is shown in Fig. 1.

Comparative Example 1 (Preparation of catalyst: catalyst composition B)

**Page 23, First Paragraph:**

A catalyst composition B was obtained as described for preparing the catalyst composition A of Example 1, except that the kneading time for catalyst forming was about 30 minutes. SEM observation shows that the maximum diameter of secondary particles of the zeolite in the formed catalyst was 10 microns. An observed SEM image is shown in Fig. 2 .

Example 3 (CT isomerization reaction)

**Page 23, Second Paragraph**

The catalyst composition A (Example 2) and the catalyst composition B (Comparative Example 1) obtained by the above method and different in the maximum diameter of secondary particles of the zeolite, the aperture of the largest pore of which comprised the 10-membered oxygen ring, in the formed catalyst were used for CT isomerization reaction tests in liquid phase. The results are shown in Table 3 below.

[Table 3] Evaluation of catalytic performance (CT isomerization reaction)

Catalyst	A (Example 2)	B (Comparative Example 1)
Reaction conditions		
Reaction temperature °C	260	260
Reaction pressure MPa-G	3. 4	3. 4
WHSV Hr	1. 5	1. 5
Reaction time Hrs	202	206
Supplied raw material		
o-CT/benzene wt/wt	2/1	2/1
o-CT isomerization rate wt%	51. 2	45. 6
CT isomer ratio wt%		
o-CT/CT	48. 8	54. 4
m-CT/CT	37. 6	33. 1
p-CT/CT	13. 6	12. 5

### Page 23, Fourth Paragraph

The catalyst composition A (Example 2) and the catalyst composition B (Comparative Example 1) obtained by the above method and different in the maximum diameter of secondary particles of the zeolite, the aperture of the largest pore of which comprised the 10-membered oxygen ring, in the formed catalyst were used for o-DCB isomerization reaction tests. The results are shown in Table 4 below.

[Table 4] Evaluation of catalytic performance (DCB isomerization reaction)

Catalyst	A (Example 2)	B (Comparative Example 1)
Reaction Conditions		
Reaction temperature °C	350	350
Reaction pressure MPa-G	2. 9	2. 9
WHSV Hr <sup>-1</sup>	4. 0	4. 0
Reaction time Hrs	24	24
o-DCB conversion percentage wt%	68. 2	57. 9
Reaction product wt%		
CB	0. 01	0. 02
o-DCB	31. 77	42. 13
m-DCB	46. 50	41. 43
p-DCB	21. 72	16. 42
ΣDCB	99. 99	99. 98

**On Page 24, Second Paragraph:**

The raw material obtained by nitrogen bubbling of o-DCB for removing oxygen (dissolved oxygen content nearly 0 ppm, measured by a polarographic dissolved oxygen meter) was treated to be dehydrated by a molecular sieve, and brought into contact with the catalyst composition A, for a liquid phase isomerization reaction test. The reaction conditions are shown in Table 5 below.

[Table 5]

Reaction temperature °C	324
Reaction pressure MPa-G	3.9
WHSV Hr <sup>-1</sup>	0.4

**On Page 24, Fourth Paragraph:**

An isomerization reaction test was carried out as described in Example 5, except that

o-DCB saturated with air (dissolved oxygen content about 40 ppm, measured by a polarographic dissolved oxygen meter) was used as the raw material. The results are shown in Fig. 3 and Table 6 below.

[Table 6]

	Dissolved oxygen content of raw material	Catalyst degradation rate
Example 5	0 ppm	0.33%/day
Comparative Example 2	Approx. 40 ppm	0.63%/day

**On Page 33, Second Paragraph:**

Seven catalyst compositions C (Example 10) through I (Comparative Example 3) prepared as described above were tested in DCT isomerization reaction. The results are shown in Table 7 below.

[Table 7] Evaluation of catalytic performance (DCT isomerization reaction)

Catalyst	Supplied raw material	C (Example 10)	D (Example 10)	E (Example 11)	F (Example 11)	G (Example 12)	H (Example 13)	I Comparative Example 3)
Reaction conditions								
Reaction temperature °C		320	320	320	320	335	330	345
Reaction pressure MPa-G		8.9	8.9	8.9	8.9	8.9	8.9	8.9
H/DCT mole/mole		0.06	0.06	0.06	0.06	0.06	0.06	0.06
WHSV Hr <sup>-1</sup>		2.0	2.0	2.0	2.0	2.0	2.0	2.0
Reaction time Hrs		140	144	136	150	146	140	150
Reaction product wt%								
Benzene, toluene, xylene		0.21	0.19	0.18	0.18	0.22	0.21	0.23
Chlorobenzene		0.49	0.52	0.50	0.45	0.56	0.54	0.64
Chlorotoluene		1.01	0.80	0.77	0.90	0.82	0.77	1.04
Dichlorobenzene		1.14	1.08	1.04	0.96	1.24	1.21	1.31
Dichloro-xylene	1.13	2.46	2.42	2.40	2.32	2.63	2.59	3.07
ΣCEB	98.87	94.69	94.99	95.11	95.19	94.53	94.68	93.71
DCT isomer ration wt%								
2, 5-DCT/DCT	45.03	39.07	38.60	38.72	38.19	38.90	38.32	38.52
2, 6-DCT/DCT	0.88	6.33	6.78	6.64	7.00	6.39	6.98	6.71
3, 5-DCT/DCT	11.26	12.59	12.70	12.63	12.65	12.68	12.77	12.56
2, 4-DCT/DCT	34.35	31.75	31.51	31.58	31.43	31.66	31.27	31.63
3, 4-DCT/DCT	3.84	4.74	4.85	4.86	5.10	4.80	5.00	4.98
2, 3-DCT/DCT	4.64	5.52	5.56	5.57	5.63	5.56	5.66	5.60

**On Page 33, Fourth Paragraph:**

The catalyst composition F (Example 11) was tested in CEB isomerization reaction, and the results are shown in Table 8 below.

[Table 8] Evaluation of catalytic performance (CEB isomerization reaction)

Catalyst	Supplied raw material	F (Example 11)
Reaction conditions		
Reaction temperature °C		245
Reaction pressure Mpa-G		4.0
H/DCT mole/mole		0.06
WHSV Hr <sup>-1</sup>		1.3
Reaction time Hrs		188
Reaction product wt%		
Low boiling point compounds		0.02
Benzene		0.10
Ethylbenzene	0.21	0.38
Chlorobenzene	0.06	0.61
ΣCEB	99.73	95.79
High boiling point products		2.10
CEB isomer ratio wt%		
o-CEB/CEB	53.13	31.96
m-CEB/CEB	8.70	48.12
p-CEB/CEB	38.17	19.92
CEB recovery rate wt%		96.05

## In the Claims

### **Kindly add new Claims 22-26**

22. (New) A method for isomerizing halogenated aromatics comprising contacting a catalyst composition comprising a zeolite selected for isomerizing halogenated aromatics, wherein said composition further comprises a formed catalyst having secondary zeolite articles each with a maximum diameter of 5 microns or less with halogenated aromatics.

23. (New) An isomerization method comprising contacting halogenated aromatics containing 15 ppm or less of dissolved oxygen with a zeolite-containing catalyst.

24. (New) The isomerization method according to claim 23, wherein before the halogenated aromatics are contacted with said zeolite-containing catalyst, said halogenated aromatics are treated by a treatment method selected from the group consisting of dissipation treatment, reduced pressure treatment and distillation treatment, to remove the dissolved oxygen.

25. (New) The isomerization method according to claim 23, wherein the zeolite-containing catalyst is a catalyst composition comprising a zeolite selected for isomerizing halogenated aromatics, wherein said composition further comprises a formed catalyst having secondary zeolite articles each with a maximum diameter of 5 microns or less.

26. (New) The isomerization method according to claim 24, wherein the zeolite-containing catalyst is a catalyst composition comprising a zeolite selected for isomerizing halogenated aromatics wherein, said composition further comprises a formed catalyst having secondary zeolite articles each with a maximum diameter of 5 microns or less.

**Remarks**

We have canceled Claims 1-21 in favor of newly added method Claims 22-26. Those claims have been added to place them into proper form and are substantively the same as Claims 18-21, respectively. We have also amended the specification, abstract and title to place them into better form for examination on the merits and to correct minor typographical and grammatical errors. No new matter has been added.

A substitute specification is enclosed which incorporates the changes made by Preliminary Amendment. No new matter has been added.

We respectfully request passage to the appropriate art unit for examination on the merits.

Respectfully submitted,



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